Supporting Information

Interface Enables Faster Surface Reconstruction in a Heterostructured Co-Ni-S Electrocatalyst towards Efficient Urea Oxidation

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Experimental Details

Materials

All chemicals are of commercial analysis grade and used without further purifications.

Potassium hydroxide (KOH, 85%), hydrochloric acid (HCl, 36.0~38.0%), ammonium solution (NH₃·H₂O, 25.0~28.0%), cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, 98.5%), nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 98.5%), acetone absolute (C₃H₆O, 99.5%), thiourea (CH₄N₂S, TU, 99%), ethylenediamine tetraacetic acid disodium salt dihydrate (C₁₀H₁₄N₂Na₂O₈·2H₂O, EDTA, 99%) and ethanol absolute (C₂H₅OH, EtOH, 99.7%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Sodium Ruthenium (IV) oxide hydrate (RuO₂, 99%) was purchased from Urchem. Urea (CO(NH₂)₂, 99.5%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.. Nickel foam (NF) and carbon cloth (CC) with a thickness of 0.2 mm were purchased from Sigma-Aldrich. Deionized water (DI-water) (18.25 MΩ cm⁻¹) was produced by a Water Purifier system.

Synthesis of catalysts

Co-Ni-S@NF was synthesized through a one-step solvent-thermal method. Firstly, a slice of NF $(2*4 \text{ cm}^2)$ was washed with the aqueous hydrochloric acid solution (3M), ethanol, and acetone by ultrasonic treatment for 15 min, sequentially. Secondly, a solid mixture of Co(NO₃)₂·6H₂O (0.366 g), Ni(NO₃)₂·6H₂O (0.366 g) and TU (0.583 g) were dissolved in 60 mL DI-water with stirring. Then, EDTA (0.66 g) was also added and kept string for 10 min, after the mixture solution turned into transparence, 1 mL NH₃·H₂O was dropped into the uniform solution to adjust its pH value to 8. Finally, the mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave, along with the as-prepared NF. After being heated at 130 °C for 9 h, the obtained sample was washed with DI-water and ethanol for several times, then dried at 60 °C overnight and stored in the desiccator for further measurement.

The similar procedure was adopted for the preparation of Co-S@NF and Ni-S@NF, except using single metal salt of $Co(NO_3)_2 \cdot 6H_2O$ (0.732 g) and $Ni(NO_3)_2 \cdot 6H_2O$ (0.732 g), respectively. Co-S@CC was also synthesized by the same method except using carbon cloth (CC) and single metal salt of $Co(NO_3)_2 \cdot 6H_2O$ (0.732 g).

Characterizations

Scanning electron microscopy (SEM) and corresponding energy dispersive spectroscopy (EDS) images were acquired from TESCAN MIRA3 microscope equipped with TESCAN EssenceTM EDS. X-ray diffraction (XRD) was carried on a Bruker D8 DISCOVER A25 using Co source. X-ray photoelectron spectroscopy (XPS) was conducted on a PHI 5000 VersaProbe III. The spectra were corrected using C1s peak (284.8 eV) as a reference. The TEM samples of catalysts were prepared by exfoliating the composites from the NF matrix via ultrasonication treatment with ice bath for 1.5 h. A FEI Themis Z Double Cs corrector transmission electron microscope (Cs-TEM) was utilized to characterize the samples and acquire the morphological and structural information in nanoscale. Tapping-mode atomic force microscopy (TM-AFM) was applied to quantitatively analyze the thickness of the exfoliated Ni₃S₂ nanogear and Co₉S₈ nanosheet (Bruker, Dimension Icon). N₂ adsorption isotherm curves were collected on an ASAP 2460 Version 3.01, and a liquid nitrogen bath (77 K) was applied for the measurements. Inductively coupled plasma-optical emission spectrometry (ICP-OES) tests were conducted on an Agilent 5110 (OES).

In-situ Raman measurements

Renishaw's inVia Raman microscope was applied to collect the Raman spectra with the laser wavelength of 532 nm and a configuration of numerical aperture of 0.55 with $50 \times$ microscope objective was used in all Raman measurements. A home-made flow cell equipped with a slice of catalysts attached to copper conductive tape as the working electrode, Ag/AgCl as reference electrode and graphitic rod as counter electrode was utilized to collect *in-situ* Raman spectra, with the examined sample at the top facing to the objective lens. Raman spectra were acquired under controlled electrochemical potentials. Each measurement was conducted after holding at the specific potential for 120 s. The electrolyte was 1M KOH with the addition of 0.33M urea. The *in-situ* electrochemical setup and cell are displayed in Figure S24.

In-situ attenuated total reflectance Fourier transform infrared spectroscopy measurements.

The *in-situ* electrochemical infrared spectra were recorded on a Nicolet iS50 FT-IR Thermo Fisher spectrometer with silicon as the prismatic window. A thin layer of gold film was chemically deposited on the surface of the silicon prismatic prior to each experiment to improve the signal intensity. The electrolytic cell was a department cell composed of as-prepared catalyst as working

electrode, Ag/AgCl as reference electrode and Pt wire as counter electrode. 30 mL of 1M KOH with 0.33M urea solution was added into the cell, and FTIR spectra signals were collected under controlled electrochemical potentials in the wave number ranging between 400 cm⁻¹ to 4000 cm⁻¹. Each measurement was conducted after holding at the specific potential for 100 s. Each infrared absorption spectrum was acquired by averaging 64 scans at a resolution of 6 cm⁻¹. The background spectrum of the catalyst electrode was acquired at an open-circuit voltage before every systemic measurement. The *in-situ* experimental setup is depicted in Figure S25.

Electrochemical measurements

The electrochemical catalytic performance was evaluated using a CHI 660E workstation with a standard three-electrode configuration. The as-prepared Co-Ni-S@NF catalysts were directly applied as the working electrode, and the graphite rod and Hg/HgO (filled with 1 M KOH) electrode were used as counter electrode and reference electrode, respectively. To investigate the UOR performance, multiple measurements were conducted in 1 M KOH with 0.33 M urea aqueous solution with 95% *iR* compensation, without extra explanation. For Hg/HgO as reference electrode, the potential *E* (vs RHE) was calculated by *E* (vs RHE) = *E* (vs Hg/HgO) + 0.059pH + 0.098 V. The similar configuration was utilized to evaluate the OER performance except using a mixture solution of 1 M KOH as electrolyte. To prepare RuO₂@NF benchmark electrode, RuO₂ catalysts inks were prepared by dispersing 10 mg of purchased commercial RuO₂ powder into 2 mL ethanol containing 100 µL of 5 wt% Nafion via ultrasonication treatment for at least 1h with ice bath. Then 100 µL of the catalyst ink was loaded onto a treated NF with geometric area of 1 cm², the loading amount of RuO₂ was ~0.25 mg cm⁻².



Figure S1. SEM images under low- and high- magnifications of Co-Ni-S@NF.



Figure S2. Atomic force microscope (AFM) images of Co-Ni-S@NF.



Figure S3. (a) Cyclic voltammograms of Ni-S@NF in 1 M KOH and 0.33 M urea solution at different scan rates. (b) Plot of the logarithm of cathodic peak current density (j_c) against the logarithm of scan rate (v).

Given the power law relationship between the cathodic peak current density (j_c) and the scan rate (v): $j_c = av^{b}$.^[1] The logarithm of the current density of the cathodic peak was plotted against the logarithm of the scan rates to extract the exponent b value of redox process. In the two limiting cases: (i) b = 0.5 when it is a diffusion-controlled redox process; (ii) b = 1 when it is a perfectly non-diffusion-controlled capacitive behavior. The extracted exponent b value of cathodic peak is 0.639± 0.0195, indicating the redox feature is associated with a mixed control of diffusion and capacitive behavior, similar to Co-Ni-S@NF.



Figure S4. Structural and compositional Characterizations and electrochemical performance of Co-S@NF. (a) XRD pattern. (b) HRTEM image. (c-d) SEM images under c) low- and d) high- magnifications and its corresponding EDS images. (e) LSV curves for UOR of various catalysts in 1.0 M KOH that contains 0.33 M urea at a scan rate of 5 mV s⁻¹.



Figure S5. SEM images under low- and high- magnifications and its corresponding EDS images of Co-S@CC.



Figure S6. Electrochemical urea oxidation reaction (UOR) performance of NF. (a) LSV curve for UOR in 1.0 M KOH + 0.33 M Urea at a scan rate of 5 mV s⁻¹. (b) Tafel plot. (c) C_{dl} obtained by CV curves at given scan rates. (d) CV curves of NF in the non-faradic potential region (-0.4 to -0.3 V vs. Hg/HgO) at various scan rates (10 to 100 mV s⁻¹).



Figure S7. CV curves of (a) Co-Ni-S@NF, (b) Ni-S@NF, (c) Co-S@CC and (d) S-NF, in the non-faradic potential region (-0.4 to -0.3 V vs. Hg/HgO) at various scan rates (10 to 100 mV s⁻¹).



Figure S8. Electrochemical oxygen evolution reaction (OER) performance of as-prepared selectrodes. (a) LSV curves for OER in 1.0 M KOH at a scan rate of 2 mV s⁻¹. (b) Overpotentials at current density of 100 and 200 mA cm⁻². (c) Tafel plots. (d) Amperometric i-t curve at a current density of 350 cm⁻² for Co-Ni-S@NF catalyst.



Figure S9. Structural and compositional characterizations of S-NF. (a-e) SEM images under low- and high- magnifications and its corresponding EDS images. (f) HRTEM image. (g) HAADF and its corresponding EDS elemental mapping images.



Figure S10. Structural and compositional characterizations of Ni-S@NF. (a-e) SEM images under low- and high- magnifications and its corresponding EDS images. (f) HRTEM image. (g) HAADF and its corresponding EDS elemental mapping images.



Figure S11. N₂ adsorption profiles for pre-catalysts.



Figure S12. XPS survey spectrum (a) and high-resolution XPS spectrum for O 1s (b) of Co-Ni-S@NF.



Figure S13. Hybrid model between Co₉S₈ and Ni₃S₂ phase for Co-Ni-S@NF heterointerface.



Figure S14. Single metal sulfide model of (a) Ni₃S₂ and (b) Co₉S₈.



Figure S15. HAADF and its corresponding EDS elemental mapping images of (a) Ni-S@NF and (b) Co-Ni-S@NF after 50 LSV.



Figure S16. CV curves for UOR of Co-Ni-S@NF and Ni-S@NF catalysts at a scan rate of 5 mV s⁻¹.



Figure S17. HRTEM image of the Co-Ni-S@NF after OER testing.



Figure S18. HAADF and its corresponding EDS elemental mapping images of post-UOR Co-Ni-S@NF.



Figure S19. HAADF and its corresponding EDS elemental mapping images of post-OER Co-Ni-S@NF.



Figure S20. High-resolution XPS spectrum for S 2p of Co-Ni-S@NF after UOR testing.



Figure S21. High-resolution XPS profiles for (a) Ni 2p, (b) Co 2p, (c) O 1s, and (d) S 2p of Co-Ni-S@NF after OER testing.

The surface chemical status of post-OER Co-Ni-S@NF catalyst was also investigated by XPS spectra. As depicted in Figure S21, the existence of Ni, Co, and O was proved for the sample after OER testing while sulfur on the sample surface has almost not been detected, which is the same as the post-UOR sample. After OER testing, the peaks corresponding to Ni and Co species were moved to higher binding energy in position, which indicates a higher oxidation state. The change of characteristic binding energy peak in position and intensity for the elements demonstrated the electronic structure evolution during the surface self-reconstruction process, which could have an impact on the electrocatalytic performance of the Co-Ni-S@NF electrode.



Figure S22. *In-situ* FTIR spectra at different potentials for Co-S@CC catalyst in UOR electrocatalysis.



Figure S23. Formation energy of S defect between different models.



Figure S24. Experimental setup for *in-situ* **Raman testing.** The experimental setup (a) and the cell (b) for *in-situ* Raman measurements.



Figure S25. Experimental setup for *in-situ* **ATR-FTIR testing.** The experimental setup (a) and the cell (b) for *in-situ* ATR-FTIR measurements.

Catalysts	Electrolyte	Potential (V vs. RHE) for 100 mA cm ⁻²	Current density (mA cm ⁻²) @ 1.4V	Stability	Reference
Co-Ni-S@NF	1.0M KOH + 0.33M Urea	1.35	349	100h	This work
V ₂ O ₃ /Ni/NF	1.0M KOH + 0.5M Urea	1.40	100	20h	[2]
Ni-WO _x	1.0M KOH + 0.33M Urea	1.42	~90	10h	[3]
O-NiMoP/NF	1.0M KOH + 0.5M Urea	1.41	~90	40h	[4]
$Co_2Mo_3O_8$	1.0M KOH + 0.5M Urea	1.40	100	20h	[5]
Ni ₂ Fe(CN) ₆	1M KOH+ 0.33 M Urea	1.35	255	2000s	[6]
MoP@NiCo- LDH/NF-20	1.0M KOH + 0.5M Urea	1.39	~110	20h	[7]
Ni(OH)2@NF	1M KOH+ 0.3 M Urea	1.44	~85	40h	[8]
CoFeCr LDH	1M KOH+ 0.33 M Urea	1.41	~85	20h	[9]
NiClO-D	1M KOH+ 0.33 M Urea	1.44	~60	100h	[10]
$Ni_{0.9}Fe_{0.1}O_x$	1M KOH+ 0.33 M Urea	1.40	~101	25h	[11]
Ni-Mo	1M KOH+ 0.1M Urea	1.42	~65	24h	[12]
1%Cu: Ni(OH) ₂	1M KOH+ 0.33M Urea	1.41	~85	40h	[13]

Catalysts	Metal Loading (mg cm ⁻²)
Co-Ni-S@NF	2.85
Ni-S@NF	2.85
Co-S@CC	2.8

 Table S2. Metal loading of different pre-catalysts.

Table S3. Ion content of composed elements of Co-Ni-S@NF catalyst before UOR testing.

Element	Ion content (ppm)
S	77.6
Со	42.8
Ni	4105.2

Table S4. Ion content of composed elements of Co-Ni-S@NF catalyst after UOR testing.

Element	Content (ppm)
S	46.8
Со	18.8
Ni	4079.2

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